

FORMATION OF HYDROCARBONS FROM $H_2 + CO$ IN MICROWAVE-GENERATED ELECTRODELESS DISCHARGES

Bernard D. Blaustein and Yuan C. Fu

U. S. Bureau of Mines, Pittsburgh Coal Research Center,
4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213

Formation of hydrocarbons from $H_2 + CO$ over metal catalysts is of considerable interest and has been studied at length. Hydrocarbons can also be formed in electrical discharges,^{3, 5-9, 11-17/} and this offers an interesting alternative for producing hydrocarbons from $H_2 + CO$. Fischer and Peters^{5/} worked with a flow system where the gases at 10 torr pressure circulated through a discharge (50 Hz) between metal electrodes, then through a mercury vapor pump, a liquid air-cooled trap, and back to the discharge. Conversion of CO to hydrocarbons was very low for one pass through the discharge, but by recirculating the gases for 100 minutes, practically all of the CO would react.

Lunt^{9/} and Epple and Apt^{3/} worked with electrodeless radiofrequency (2-110 MHz) discharges in static reactors at pressures up to 300 torr. Conversions of $H_2 + CO$ and $H_2 + CO_2$ to CH_4 were quite high for reaction times of several minutes; no other hydrocarbons were formed. McTaggart,^{11/} and Vastola et al.^{16/} working with electrodeless microwave (2450 MHz) discharges in flow systems at pressures of a few torr formed only traces of hydrocarbons from $H_2 + CO$. Here, the gas passed through the discharge only once, and the residence time was a fraction of a second. However, work in our laboratory has shown that in a static reactor, and with reaction times of the order of a minute, CO can be converted in high yields to hydrocarbons in an electrodeless microwave discharge in $H_2 + CO$, under conditions where essentially no polymers are formed.

EXPERIMENTAL PROCEDURES

Reactions were carried out in 11-mm ID cylindrical Vycor reactors placed in a coaxial cavity (Ophthos Instruments, similar to type 2A described by Fehsenfeld et al.^{4/}) connected by a coaxial cable to a Raytheon KV-104A CMD-10 2450 MHz generator. For a run, the reactors were evacuated to $< 3 \mu$ and filled with either 5:1 H_2 -CO or various H_2 -CO-Ar (typically 5.1:1.0:0.4) mixtures prepared from tank gases and stored in the vacuum system. Product analyses were made on a CEC 21-103C mass spectrometer. Net power into the discharge, measured with a Microwave Devices model 725.3 meter, was approximately 34 watts, although lower power levels could be used. Air was blown through the cavity to cool the reactor somewhat, but the estimated wall temperature in the discharge was still several hundred degrees C.

Runs with argon gave the same results as in the absence of Ar, and the ratio of total-carbon-to-argon in the product was usually a few percent lower in the product, but did not vary by more than ± 10 percent from its value in the original mixture, indicating that only negligible amounts of polymers were formed in the reaction. For $H_2 + CO$ mixtures without Ar it was assumed that polymer formation was negligible, so long as reaction conditions were similar.

As a precaution against the gradual accumulation of small amounts of polymer in the reactors, they were cleaned before each run by maintaining a discharge in O_2 at about 10 torr for 3 minutes to oxidize any carbonaceous material present. This was repeated twice, with fresh samples of O_2 . A discharge in H_2 (about 10 torr) was then maintained for 3 minutes in the reactor. This was also repeated twice, with fresh samples of H_2 . Since the reactions to be studied were to be carried out in a reducing environment, this treatment with H_2 was felt to be desirable after the O_2 discharge.

RESULTS

Figure 1 shows the results of experiments made at initial gas pressure of 12 ± 1 torr in 36-cm long by 11-mm ID reactors. The percent of carbon present in the product as C_2H_2 and as $CH_4 + C_2H_2$ is plotted vs. reaction time. Figure 2 shows the percent of carbon present in the product as CH_4 for the same runs. Water, CO_2 , and occasionally slight traces of other hydrocarbons, were also present in the product. The conversion of CO to $CH_4 + C_2H_2$ reaches a maximum of 17-18% for reaction times of 30-120 seconds. Figure 3 shows the results of experiments made at initial gas pressures of 50 ± 3 torr in 20-cm long by 11-mm ID reactors. Here, the percent of carbon present as $CH_4 + C_2H_2$ is at a maximum of 24-25% for reaction times of 3-4 minutes. There is considerable scatter in the data; the dashed curves are intended to show only the general trend.

These data show that conversion of CO to hydrocarbons in the discharge under these conditions is limited. The composition of the gases in the reactor approaches a stationary state, for reaction times of the order of 0.5 to 3 minutes, depending upon the pressure. Because of the geometry of the reactors, and the volume of a reactor relative to the volume occupied by the discharge, the time required to reach the stationary state appears to be longer than is actually so, due to the relatively long times required for diffusion of gases into and out of the discharge. (The 36-cm long reactors were used for the runs made at 12 torr; for the runs made at 50 torr, the shorter 20-cm long reactors were used. Preliminary experiments showed that the conversion of CO to $CH_4 + C_2H_2$ at 50 torr in 36-cm long reactors was essentially the same as for the 20-cm long reactors, but took 1-2 minutes longer to achieve maximum conversions.)

High yields of gaseous hydrocarbons from $H_2 + CO$ have now been shown to occur in low-frequency (50 Hz^{5/} and 60 Hz^{17/}) discharges, radiofrequency (2-110 MHz)^{3/} and microwave (2450 MHz) discharges. However, in all of these cases, the reaction does not appear to be an extremely rapid one, such as is the case for dissociation of diatomic molecules in a discharge, for instance.

For reaction times longer than those needed to reach maximum conversions, the conversions appear to decrease. This is probably due to some polymer formation, but not enough to show up as a 10% decrease in the analytically determined C/Ar ratio. Several runs at 12 torr (not plotted) of 5 minutes duration, and some longer runs, including one at 50 torr for 10 minutes, gave values of the C/Ar ratio more than 10% below the initial value of the ratio, and this was considered evidence of polymer formation. Here, also, the yields of CH_4 and C_2H_2 were lower.

Conversions of CO could be increased by removing reaction products as they formed, by having a cold trap surround the bottom 5 cm of the reactor before and during the time that the discharge was maintained at a distance of 10 cm from the bottom. The discharge is localized and extends over a distance of about 2 cm. As shown in table 1, the conversion of CO increased markedly and the product distribution changed. Values for the C/Ar ratio indicated that polymers were not formed. Also, there is no indication that the product distribution is any different in the presence of Ar than in its absence. The first three columns in the table are for the 3-minute runs shown in figures 1 and 2. When the discharge was maintained for 3 minutes or longer, with Dry Ice (-78°) surrounding the end of the reactor, the percent of carbon present in the final product as CH_4 is 51%; C_2H_2 , 17%; C_2H_6 , 10%. At this temperature, the only reaction product frozen out is H_2O . Apparently, the removal of this is sufficient to increase the conversion of CO to hydrocarbons to approximately 78%.

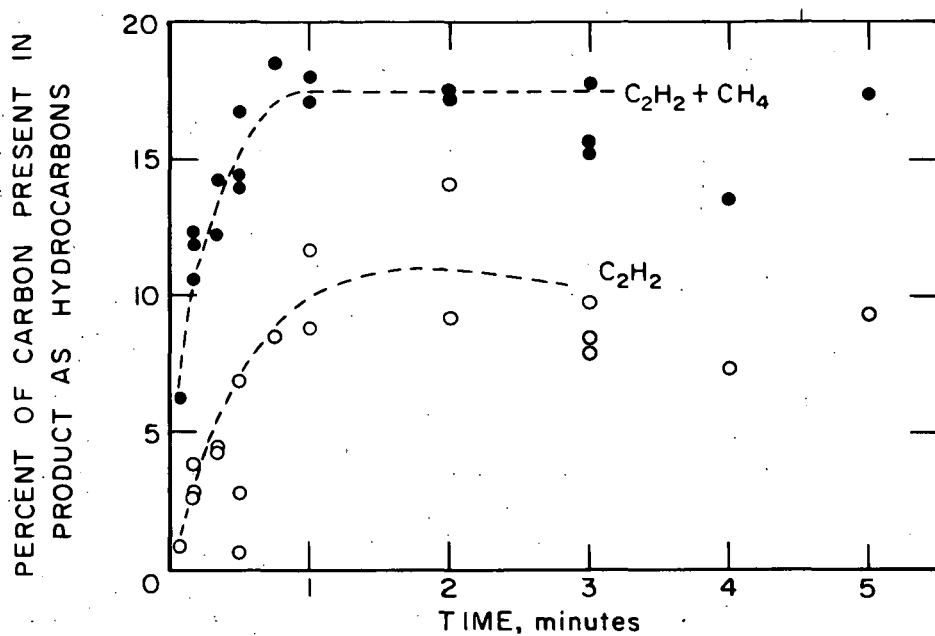


Figure 1.—Formation of hydrocarbons from $H_2 + CO$ in microwave-generated discharge: acetylene \circ , acetylene + methane \bullet . Initial gas pressure = 12 ± 1 torr.

11-30-66

L-9694

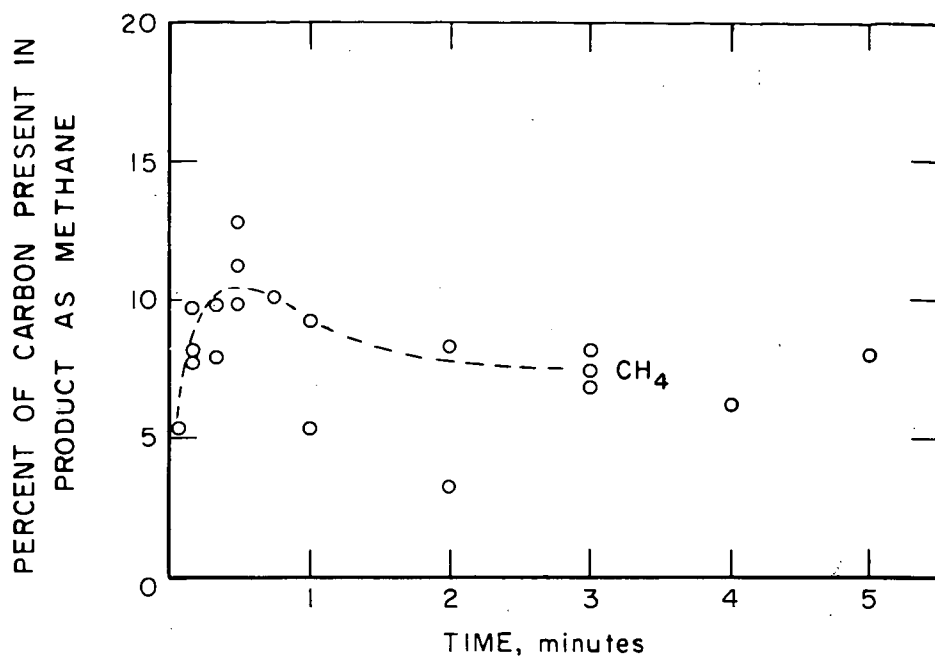


Figure 2.—Formation of CH_4 from $\text{H}_2 + \text{CO}$ in microwave-generated discharge. Initial gas pressure = 12 ± 1 torr.

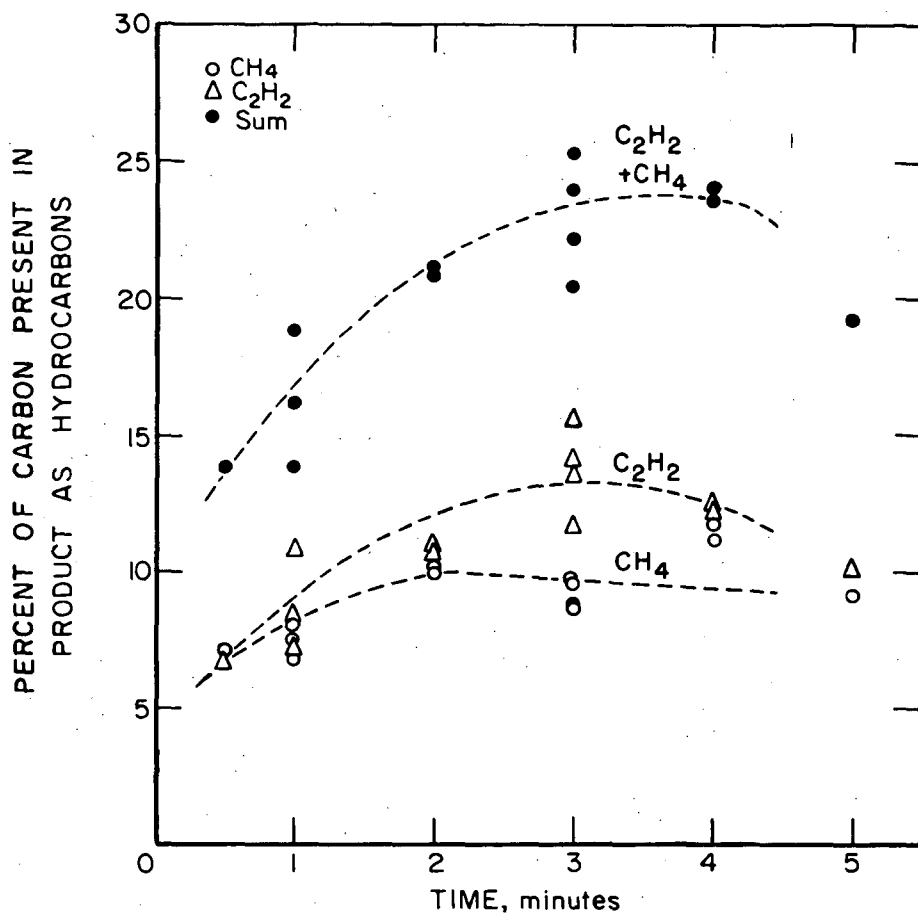


Figure 3.—Formation of hydrocarbons from $H_2 + CO$ in microwave-generated discharge: methane ○, acetylene △, acetylene + methane ●. Initial gas pressure = 50 ± 3 torr.

TABLE 1. - Conversion of CO to hydrocarbons in a microwave discharge:
No cooling vs. cooling the bottom of the reactor

Conditions	Run:	6294	10252	10253	9232	11012	7154	7153	8129	10213	11011	9233	9025	8192	10211	7071
Cooling bath, °C		None	None	None	-78	-78	-78	-196	-196	-196	-196	-196	-196	-196	-196	-196
Time, min		3	3	3	3	3	3	3	3	3	3	3	2	3	3	5
Pressure, torr		12.0	12.8	12.0	12.6	12.4	12.0	11.2	12.5	11.9	13.0	12.0	12.4	12.6	51	52
H ₂ /CO		5.1	5.1	5.1	5.0	5.1	5.1	5.1	5.1	5.1	5.1	5.0	2.2	2.2	5.1	5.1
Argon		Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	Yes	Yes
Percent carbon present in product as																
CH ₄		6.8	8.1	7.4	52.0	50	51.0	3.4	4.8	4.0	3.9	3.4	1.0	.6	3.9	3.7
C ₂ H ₂		8.5	9.7	7.9	19.9	15	17.2	5.7	48.6	2.9	19.7	4.8	46.3	32.9	61.8	55.6
C ₂ H ₆		-	-	-	7.8	9	12.6	79.2	31.0	75.7	63.6	75.8	35.6	46.6	.4	.5
C ₃ + C ₄		-	-	-	trace	trace	trace	3.6	8.8	8.9	2.0	8.7	3.2	10.0	-	-
CO ₂		2.1	1.4	2.1	trace	+	-	4.2	4.0	4.1	5.3	4.3	9.4	9.6	2.4	2.5
Hydrocarbons		15	18	15	80	74	81	92	93	92	89	93	86	90	66	60

The next five columns in table 1 show that with liquid N_2 cooling (-196°), the percent of carbon in the product as CH_4 in only 4%; $C_2H_2 + C_2H_6$ (with the latter predominating) 81%; $C_3 + C_4$ hydrocarbons, 6%; more H_2O and CO_2 are also formed. The mass spectrometric analyses indicated that traces of oxygenates were also present in the products of these runs, but in such small amounts that no identifications could be attempted. For some unknown reason, C_2H_4 is not formed under these conditions. (Several runs were analyzed by gas chromatography for C_2H_4 and none was found.) At a temperature of -196° , the only non-condensables present in the mixture are H_2 , CO , and CH_4 ; all the other products are frozen but. One can speculate that the high yield of C_2H_6 is due either to a recombination of CH_3 radicals at the cold surface, or hydrogenation of C_2H_2 , but the mechanism of formation of any of the hydrocarbon products is not known.

The next-to-last pair of columns in table 1 show that very high conversions of CO to C_2 - and higher hydrocarbons can be obtained using a 2.2:1 $H_2 + CO$ mixture. Here, also, the CO_2 production is higher, and the CH_4 lower, than compared with the more hydrogen-rich reactant mixture. The last pair of columns, giving data for runs made at 50 torr, indicate that C_2H_2 was, by far, the predominant product in these runs.

The almost complete conversion of CO to hydrocarbons, H_2O , and CO_2 , obtained by cooling the bottom of the reactor, is reversible. Several additional experiments (at 12 torr), where the gases were reacted for 3 minutes while the reactor was cooled, the bottom of the reactor then warmed to room temperature in a few seconds with a water bath, and the gases reacted for 2 more minutes, gave the same product compositions as for the runs shown in figures 1 and 2.

Table 2 gives the results of some preliminary experiments where water vapor was added to the $H_2 + CO + Ar$ mixture before reaction. The water vapor was added to the previously evacuated reactor and a portion of the vacuum system connected to a Pace Engineering Co. Model P7 pressure transducer containing a ± 1 psi diaphragm. The output of this was indicated on a Pace Model CD25 transducer indicator. After the water vapor partial pressure was measured, the stopcock to the reactor was closed and the water frozen at the bottom of the reactor. The reactor was then filled with the H_2 - CO - Ar mixture, the bottom of the reactor warmed slightly, and 3 minutes allowed for mixing of the gases before the discharge was initiated.

Even from these few experiments, it can be seen that adding water vapor to the initial reactant mixture has a strong inhibitory effect on the production of hydrocarbons. (The CO_2 yield is increased due to the reaction $H_2O + CO \rightarrow CO_2 + H_2$.) Comparison of the second and third runs listed in the table shows that 3 minutes reaction time increases the yield of hydrocarbons only slightly as compared to one minute. The last two runs in the table show that when the water vapor partial pressure is equal to or greater than the CO partial pressure in the reactant gas mixture, no hydrocarbons are produced at all.

The pronounced inhibitory effect of H_2O vapor on hydrocarbon formation in this reaction may explain some of the scatter of the data shown in figures 1, 2, and 3. It is possible that small (and variable) amounts of H_2O vapor were adsorbed on the walls of the reactor tubes, and that this decreased the hydrocarbon yield in (some of) the runs by a varying amount which shows up as scatter in the data. Further experiments would have to be done to shed more light on this point. However, there are other, as yet unknown, sources of variability in the experimental conditions which also undoubtedly contribute to the scatter in the data.

TABLE 2. - Effect of adding water to the H₂-CO-Ar mixture.
Repression of hydrocarbon formation

	Run 11153	11151	11154	11152	11013
Initial H ₂ -CO-Ar (5.1:1.0:0.4) pressure torr	10.8	12.6	13.9	11.8	12.7
Initial H ₂ O pressure added, torr	.35	.85	.95	1.83	6
Time of discharge, min.	1	1	3	1	1
Percent of carbon present in product as					
CH ₄	4.0	1.9	1.7	0.0	0.0
C ₂ H ₂	4.2	1.8	2.6	0.0	0.0
CO ₂	3.3	4.6	4.5	8.8	23.1
Hydrocarbons	8.2	3.7	4.3	0	0

DISCUSSION

The different conversions of CO can be explained by assuming that the reaction in the discharge, without cooling the bottom of the reactor, reaches a stationary state where the production of CH₄ and C₂H₂ is limited by the back reaction of these hydrocarbons with H₂O and/or CO₂ to form H₂ + CO. The data in figure 3, by comparison with the runs in figures 1 and 2, indicate that conversion of CO to hydrocarbons is increased at higher initial pressures, as would be expected for a reaction where the volume of the products is less than the reactants. When one or more of the reaction products are removed from the discharge zone by being frozen out, the stationary state shifts and more CO reacts to form hydrocarbons. When the frozen-out hydrocarbons are re-introduced into the discharge, they react very readily to re-form the initial stationary state composition. If, on the other hand, water vapor is added to the initial reactant gas mixture, the conversion of CO to hydrocarbons is repressed.

These experimental observations can be summed up by discussing the reaction $H_2 + CO \rightarrow CH_4 + H_2O$ in terms of a stationary state in the discharge which can shift in the direction that would be predicted by applying Le Chatelier's principle. Actually, in this respect, the system behaves as if it were in chemical equilibrium. Qualitatively, this interpretation of the data is very reasonable. Fischer and Peters,^{5/} Wendt and Evans,^{12/} Lunt,^{9/} and Epple and Apt^{3/} have all discussed the production of hydrocarbons from H₂ + CO in terms of equilibria in the discharge. However, simple arguments show that any discussion of equilibria in discharges is not a straightforward one because of the absence of temperature equilibria among the various species - electrons, ions, and molecules - in the discharge.^{1/}

Manes^{10/} has pointed out that in the statistical mechanical derivation of the equilibrium constant in terms of the partition functions, the functional form of the equilibrium constant expression follows from the conservation of atoms in the system. This leads to the likelihood that the H₂-CO-CH₄-H₂O-CO₂ system will conform to some equilibrium "constant" in an electrical discharge system, although the magnitude of this constant will not be derivable from equilibrium thermodynamic properties.

Given the existence of this equilibrium "constant" for (some) reactions occurring in a discharge, we would then expect Le Chatelier's principle to apply. In fact, the "constant" need be only approximately constant, as conditions change over a certain range, for the system to exhibit qualitative changes in accordance with Le Chatelier's principle.

For a preliminary inspection of the quantitative aspects of these equilibria "constants," from the data in table 2 and the two one-minute runs in figures 1 and 2, values were calculated for

$$K_1 = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}}$$

and

$$K_2 = \frac{P_{CH_4} \times P_{H_2O}}{P_{CO} \times P_{H_2}^3}$$

These are given in table 3. If these equilibria had been established in an ordinary thermal system, the values for K_1 and K_2 would depend only on temperature. However, these "equilibria" were established in a reactor system where part of the gas was in an electrical discharge. Since we cannot define one temperature for the discharge, the experimental values obtained for K_1 and K_2 depend on the parameters which characterize the discharge, such as rate of energy input, geometry of the reactor, the volume of gas in the discharge relative to the volume of the reactor, and the electrical variables, such as field strength, etc.

The values obtained for K_1 and K_2 can be used to define a "chemically equivalent temperature" for the gases in the discharge. Thus, the average value for K_1 corresponds to a "temperature" of 1300°K. This is very approximate, due to the small change of K with temperature for this reaction near 1300°K. The average value for K_2 corresponds to a "temperature" of approximately 800°K. Pursuing much the same line of thought, Epplé and Apt^{3/} calculated "equivalent temperatures" of about 750°K from values of K_1 and 850°K from values of K_2 obtained from the data on the H_2 -CO- CH_4 - H_2O -CO₂ system in their static radiofrequency reactor experiments. The significance, if any, of these "temperatures" calculated from the discharge data, is unknown.

TABLE 3. - Values of equilibrium "constants" calculated from the data in table 2

Run	11153	11151	11154	11152	11013	2154	4272	"Temperature," °K
K_1	1.4	1.8	1.9	2.0	1.9	1.1	1.9	1300
K_2	21	12	9	<u>1/</u>	<u>1/</u>	22	33	800
$K_3 \times 10^3$	7.4	17	37	<u>1/</u>	<u>1/</u>	4.5	6.3	1300
K_4	3.2	2.5	3.2	<u>1/</u>	<u>1/</u>	2.1	6.9	-

^{1/} Due to the large concentration of H_2O vapor, no hydrocarbons were produced in these runs.

One unusual finding of Epple and Apt is that CH_4 was the sole hydrocarbon produced under their conditions. Even though CH_4 was present in the discharge for minutes, no C_2H_2 was produced. We have repeated their experiments (using a 400 KHz generator) and can confirm this finding, as well as their values for the amount of CO converted to CH_4 in a radiofrequency discharge. On the other hand, C_2H_2 is always produced in the reaction in a microwave discharge. In attempting to explain this difference in products in the two cases, perhaps some significance can be found in the approximate values of 1300°K calculated from K_1 for our microwave discharge runs as contrasted with 750°K from K_1 calculated by Epple and Apt. The difference in these "temperatures" may be another indication of what we feel intuitively - namely, that the microwave discharge is "hotter" than the radiofrequency discharge, because of the higher value of energy input per mole of gas in the discharge.

Values were also calculated for

$$K_3 = \frac{\frac{P}{\text{C}_2\text{H}_2} \times \frac{P^3}{\text{H}_2}}{\frac{P^2}{\text{CH}_4}}$$

and

$$K_4 = \frac{\frac{P}{\text{C}_2\text{H}_2} \times \frac{P^2}{\text{H}_2\text{O}}}{\frac{P^2}{\text{CO}} \times \frac{P^3}{\text{H}_2}}$$

and are given in table 3. From the average value for K_3 , one can calculate a "temperature" for this reaction of approximately 1300°K. The values for K_4 ($K_4 = K_2 \times K_3$) are much higher than there is any reason to expect, since for this reaction, $\log K = -4.6$ at 300°K, and decreases with increasing temperature. The values calculated for K_4 indicate that the reaction



is not even remotely near any sort of equilibrium in the discharge; the amount of C_2H_2 formed is far greater than can be accounted for at equilibrium.

In summary, it is helpful to discuss qualitatively at least some reactions in discharges from the point of view of stationary states or equilibria, which can shift according to Le Chatelier's principle. Admittedly, this approach is speculative at the moment. Other workers^{2/} are also attempting to discuss discharge reactions in terms of equilibria, and it will be of interest to see how useful these ideas prove to be in interpreting chemical reactions in discharges.

The authors wish to thank Gus Pantages, Waldo A. Steiner, and Paul Golden for their technical assistance; A. G. Sharkey, Jr. and Janet L. Shultz for the mass-spectrometric analyses; and Drs. Irving Wender and Frederick Kaufman for their valuable discussions.

REFERENCES

1. Arzimovich, L. A. Elementary Plasma Physics. Blaisdell Pub. Co., New York, N. Y., 1965, pp. 5-6.
2. Eck, R. V., E. R. Lippincott, M. O. Dayhoff, and Y. T. Pratt. *Science*, **153**, August 5, 1966, pp. 628-633.

3. Epple, R. P. and C. M. Apt. The Formation of Methane from Synthesis Gas by High-Frequency Radiation. Gas Operations Research Project PF-27(ext.), Am. Gas Assoc. Catalog No. 59/OR, Am. Gas Assoc., Inc., July 1962, 47 pp.
4. Fehsenfeld, F. C., K. M. Evenson, and H. P. Broida. Rev. Sci. Instruments, 36, March 1965, pp. 294-298.
5. Fischer, F. and K. Peters. Brennstoff-Chem., 12, No. 14, 1931, pp. 268-273.
6. Lefebvre, H. and M. van Overbeke. Chimie et Industrie, Special No., April 1934, pp. 338-342.
7. Lefebvre, H. and M. van Overbeke. Compt. rend., 198, 1934, pp. 736-738.
8. Losanitsch and Jovitschitsch in Ch. IV of "The Conversion of Coal into Oils," by F. Fischer, E. Benn, Ltd., London, 1925
9. Lunt, R. W. Proc. Roy. Soc. (London), 108A, 1925, pp. 172-186.
10. Manes, M. Private Communication.
11. McTaggart, F. K. Austral. J. Chem., 17, 1964, pp. 1182-1187.
12. Sahasrabudhey, R. H. and S. M. Deshpande. Proc. Indian Acad. Sci., 31A, 1950, pp. 317-324.
13. Sahasrabudhey, R. H. and S. M. Deshpande. J. Indian Chem. Soc., 27, 1950, pp. 361-368.
14. Sahasrabudhey, R. H. and S. M. Deshpande. J. Indian Chem. Soc., 28, 1951, pp. 377-382.
15. Sahasrabudhey, R. H. and A. Kalyanasundaram. Proc. Indian Acad. Sci., 27A, 1948, pp. 366-374.
16. Vastola, F. J., P. L. Walker, Jr., and J. P. Wightman. Carbon, 1, No. 1, 1963, pp. 11-16.
17. Wendt, G. L. and G. M. Evans. J. Am. Chem. Soc., 50, 1928, pp. 2610-2621.